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3,476,563

PHOTOGRAPHIC SILVER HALIDE ELEMENTS CONTAINING TWO EQUIVALENT CYAN COUPLERS

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9 Claims

ABSTRACT OF THE DISCLOSURE

Couplers containing at least one 4-hydroxy-3-carbamyl-1-naphthyl group wherein the hydrogen atom of the one position of said naphthyl group has been replaced with an aryloxy group are used advantageously in color photography to form cyan dye images. The immediate couplers that are diffusible are used to advantage in cyan color developer solutions while the immediate couplers that are nondiffusible are advantageously incorporated in cyan dye-forming photographic emulsion layers.

This invention relates to color photography and more particularly to new and improved cyan dye-forming coupler compounds for use in image-forming systems and processes utilizing such couplers for the formation of images. In a more specific aspect, my invention relates to two-equivalent coupler compounds for forming cyan dye images in color photography.

The formation of color photographic images by the imagewise coupling of oxidized aromatic primary amino developing agents with color-forming or coupling compounds to form indoaniline, indophenol, and azomethine dyes is well known. In these processes, the subtractive process of color formation is ordinarily used and the image dyes customarily formed are cyan, magenta, and yellow, the colors that are complementary to the primary colors, red, green, and blue, respectively. Usually phenol or naphthol couplers are used to form the cyan dye image; pyrazolone or cyanacetyl derivative couplers are used to form the magenta dye image; and acylacetamide couplers are used to form the yellow dye image.

In these color photographic systems, the color-forming couplers may be either in the developer solution or incorporated in the light-sensitive photographic emulsion layer so that, during development, it is available in the emulsion layer to react with the color developing agent that is oxidized by silver image development. Diffusible couplers are used in color developer solutions. Nondiffusing couplers are incorporated in photographic emulsion layers.

Most of the couplers which have been used in the various color photographic systems described above are four-equivalent couplers, that is, they require reduction of 4 mols of silver halide for the formation of 1 mol of dye. Certain of the prior art couplers are two-equivalent couplers, i.e., they require reduction of only 2 mols of silver halide for the formation of 1 mol of dye. However, some of the prior art couplers exhibit serious disadvantages such as low reactivity, formation of an unacceptably high level of color fog, and other undesirable side reactions.

It is an object of my invention to provide new and improved two-equivalent couplers capable of forming a dye on coupling with the oxidation product of an aromatic amino developing agent.

It is another object to provide new two-equivalent couplers having a materially reduced tendency to produce unwanted color density in the non-image areas.

It is another object of this invention to provide new two-equivalent couplers with greatly reduced propensity

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to unwanted side reactions and hence higher dye yield.

It is a further object of this invention to provide new and improved two-equivalent cyan couplers which have greatly increased reactivity, thereby obviating prolonged or forced development.

It is another object of my invention to provide improved color photographic image-forming layers containing my new two-equivalent couplers dispersed in a colloidal film-forming binder.

It is another object of my invention to provide a simple, economical, and reproducible process for preparing my novel couplers in high yield.

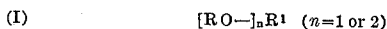
It is a further object to provide photographic silver halide-gelatin emulsion layers containing my new couplers for use in color photography.

It is another object of my invention to provide improved photographic cyan dye images by the use of these couplers.

These and other objects will appear from the following description of my invention.

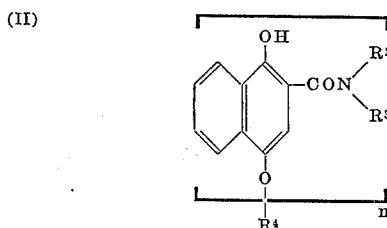
These and other objects are accomplished according to my invention by the preparation and use of my 1-hydroxy-4-aryloxy-2-naphthamide two-equivalent couplers wherein the hydrogen atom of the coupling position (i.e., 4-position) in the naphthyl nucleus has been replaced with an aryloxy radical.

The couplers of my invention include those represented by the Formula I:



wherein R represents a 4-hydroxy-3-carbamyl-1-naphthyl group and R^1 represents an aryl or an arylene (i.e., a divalent organic aromatic radical) group. Although the effectiveness of my couplers as two-equivalent couplers is not dependent on the specific composition of R and R^1 , it will be understood that these radicals may contain various substituent groups and that the character and the degree of substitution may be modified according to such requirements, e.g., spectral absorptivity, reactivity, and solubility, as may be imposed by the photographic system in which the coupler is to be used.

Accordingly, the couplers of my invention may be further represented by the following Formula II:



wherein n represents an integer of from 1 to 2, R^2 and R^3 represent any combination of hydrogen, an alkyl radical, either straight or branched chain of from 1 to 30 carbon atoms, a mono- or bicyclic alkyl radical such as cyclohexyl, terphenyl, e.g., a norbornyl radical, etc., an aryl radical such as phenyl, naphthyl, etc., a heterocyclic radical such as benzimidazolyl, benzothiazolyl, etc., or the non-metallic atoms necessary to complete a heterocyclic ring such as morpholine, pyridine, etc. These groups, i.e., alkyl, aryl, and heterocyclic as defined above, may contain substituent groups such as halogen, nitro, hydroxyl, carboxyl (such that the coupler contains ballasting groups with at least 12 carbon atoms or equivalent in a non-coupling position) amino, an aryl, a substituted amino (e.g., alkylamino, dialkylamino, anilino, N-alkylanilino, etc.), a carboxyl ester (e.g., carboalkoxy, carboaryloxy, etc.), an amido (e.g., acetamido, butyramido, ethylsulfonamido, N-methylbenzamido, N-propylbenzami-

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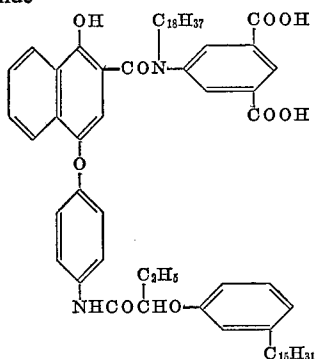
do, 4-t-butylbenzamido, etc.), a carbamyl (e.g., carbamyl, N-octadecylcarbamyl, N,N-diethylcarbamyl, N-methyl-N-phenylcarbamyl, 3-pentadecylphenylcarbamyl, etc.), a sulfamyl (such that the coupler contains ballasting groups with at least 12 carbon atoms or equivalent in a non-coupling position), (e.g., N-propylsulfamyl, N-tolylsulfamyl, etc.), an alkoxy (e.g., ethoxy, octadecoxy, etc.), an aryloxy (e.g., phenoxy, tolyloxy, naphthylloxy, etc.), sulfo, such that the coupler contains ballasting groups with at least 12 carbon atoms or equivalent in a non-coupling position, a substituted sulfonyl (e.g., methylsulfonyl, octadecylsulfonyl, ethoxysulfonyl, decoxysulfonyl, phenylsulfonyl, tolylsulfonyl, phenoxysulfonyl, etc.), etc. R^4 represents, when n represents the integer 1, an aryl group such as phenyl, naphthyl, pyridyl, quinolyl, etc., and when n represents the integer 2, R^4 represents an arylene group such as 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 1,5-naphthylene, 2,5-pyridylene, ethylene bis (1,4-phenylene), 4,4'-diphenylene sulfone, etc. These groups, i.e., aryl and arylene, may also contain substituent groups (e.g., halogen, nitro, hydroxyl, carboxyl, amino, substituted amino, carboxyl esters, amido, carbamyl, sulfamyl, alkoxy, aryloxy, sulfo, sulfonyl, etc.) as defined for alkyl, aryl, and heterocyclic in R^2 and R^3 above and phenylazo and substituted phenylazo groups.

My novel couplers are characterized by having an aryloxy group on the coupling position of the coupler which gives them good coupling reactivity and other valuable properties. These couplers are particularly characterized by the low levels of unwanted color fog, high reactivity, and good stability. Excellent coupling reactivity is obtained with couplers of my invention when incorporated in emulsion layers without the use of high-boiling coupler solvents. When high-boiling solvents are used to disperse these couplers, high dye yield and low color fog are attained over a wide range of coupler-to-solvent ratios. When the diffusible couplers of my invention are used in color developing solution, excellent reactivity and good dye yield are achieved.

Included among my novel couplers are the following typical examples which are used to illustrate but not limit my invention.

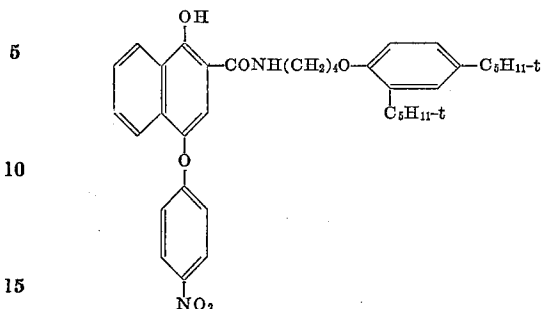
Coupler 1—1-hydroxy-4-(4-methylsulfonylphenoxy)-2-naphthamide

Coupler 2—1-hydroxy-4-{4-[α -(3-pentadecylphenoxy)butyramido]-phenoxy}-N-octadecyl-3',5'-dicarboxy-2-naphthanilide



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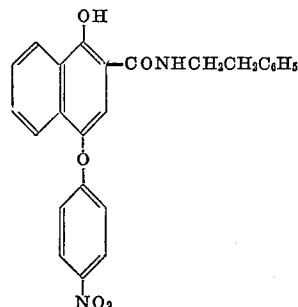
Coupler 3—1-hydroxy-4-(4-nitrophenoxy)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide



Coupler 4—1-hydroxy-4-(2,4-dinitrophenoxy)-N-ethyl-2-naphthamide

Coupler 5—1-hydroxy-4-phenoxy-2'-methoxy-2-naphthanilide

Coupler 6—1-hydroxy-4-(4-nitrophenoxy)-N-(β -phenylethyl)-2-naphthamide



Coupler 7—1-hydroxy-4-(4-acetamidophenoxy)-N-[β -(2-acetamidophenyl)ethyl]-2-naphthamide

Coupler 8—1-hydroxy-4-(pentafluorophenoxy)-N-{ β -[4-[α -(2,4-di-t-amylphenoxy)acetamido]phenyl]ethyl}-2-naphthamide

Coupler 9—1-hydroxy-4-(1-naphthylloxy)-N,N-diethyl-2-naphthamide

Coupler 10—1-hydroxy-4-(4-pyridylloxy)-4'-(4-t-butylphenoxy)-2-naphthanilide

Coupler 11—1-hydroxy-4-(4-chlorophenoxy)-2'-tetradecyloxy-2-naphthanilide

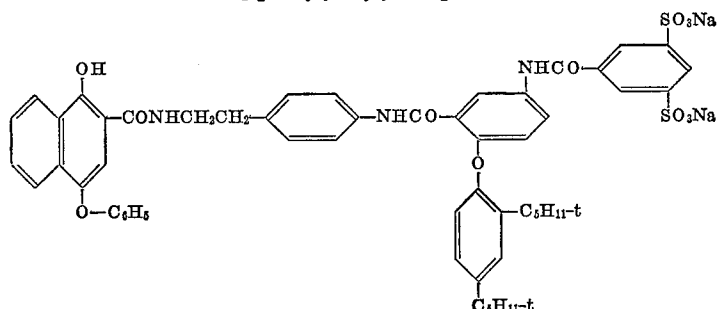
Coupler 12—1-hydroxy-4-[4-(N-methyl-N-propylsulfamyl)phenoxy]-N-octadecyl-3',5'-dicarboxy-2-naphthanilide

Coupler 13—1-hydroxy-4-[4-(4-hydroxyphenylsulfonyl)phenoxy]-3'-[α -(3-pentadecylphenoxy)butyramido]-2-naphthanilide

Coupler 14—1-hydroxy-4-(4-nitro-3-pentadecylphenoxy)-N-octadecyl-4'-sulfo-2-naphthanilide sodium salt

Coupler 15—1-hydroxy-4-(3-nitrophenoxy)-N-octadecyl-3',5'-dicarboxy-2-naphthanilide

Coupler 16—1-hydroxy-4-phenoxy-N-{ β -[4-[2-(2,4-di-t-amylphenoxy)-5-(3,5-disulfobenzamido)benzamido]-phenyl]ethyl}-2-naphthamide disodium salt

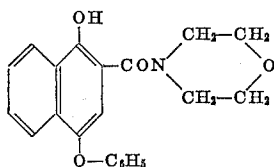


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Coupler 17—1-hydroxy - 4 - [4-(4-sulfophenylazo)phenoxy]-4' - (4-t-butylphenoxy)-2-naphthanilide sodium salt

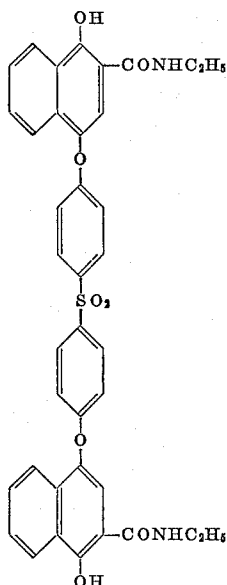
Coupler 18—1-hydroxy - 4 - (4 - sulfophenoxy)-N-octadecyl-2-naphthamide sodium salt

Coupler 19—1-hydroxy-4-phenoxy-2-naphthomorpholide



Coupler 20—1-hydroxy - 4 - (4-nitrophenoxy)-N-cyclohexyl-2-naphthamide

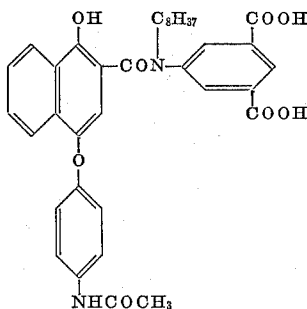
Coupler 21—4,4'-bis[4 - hydroxy-3-(N-ethylcarbamyl)-1-naphthyloxy]diphenylsulfone



Coupler 22—1,4-bis{4 - hydroxy-3-[N-(2-acetamidophenyl)carbamyl]-1-naphthyloxy}benzene

Coupler 23—1-hydroxy-4-(4 - sulfophenoxy)-N-methyl-2-naphthanilide sodium salt

Coupler 24—1-hydroxy - 4 - (4 - acetamidophenoxy)-N-octadecyl-3',5'-dicarboxy-2-naphthanilide



Coupler 25—1-hydroxy - 4 - (4-nitrophenoxy)-N-octadecyl-3',5'-disulfo-2-naphthanilide disodium salt

Coupler 26—1-hydroxy - 4 - phenoxy-N-(2-benzimidazolyl)-2-naphthamide

Coupler 27—1-hydroxy-4-(4 - nitrophenoxy)-N-methyl-N-ethyl-2-naphthamide

Coupler 28—1-hydroxy - 4 - phenoxy-N,N-(dimethyl)-2-naphthamide

The couplers of my invention are distinguished by their high reactivity and the very low density of unwanted color

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fog. The aryloxy group provides a means of attaching other substituents to my couplers such as, for example, preformed dyes useful in color correction, dye transfer processes and the like. Additional ballasting groups can conveniently be introduced via the aryloxy group; these ballasting groups are then eliminated during the coupling reaction with oxidized color developer which forms the image dyes.

The diffusible couplers of my invention, such as Couplers 1, 4, 5, 6, 7, 19, 20, 23, 26, 27, and 28 are used to advantage in color developer solutions used to color develop light-sensitive elements used for color photography which do not contain the color-forming coupler. Any of the well-known primary aromatic amino color-forming silver halide developing agents such as the phenylenediamines, e.g., diethyl - p - phenylenediamine hydrochloride, dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-diethylaminotoluene hydrochloride, 2-amino-5-(N-ethyl-N-laurylamino)toluene, N-ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline, 4-[N-ethyl-N-(β - hydroxyethyl)amino]aniline, etc., the p-amino-phenols and their substitution products where the amino group is unsubstituted may be used in the alkaline developer solution with my couplers. Various other materials may be included in the developer solutions depending upon the particular requirements, for example, an alkali metal sulfite, carbonate, bisulfite, bromide, iodide, etc., and the thickening agents used in viscous developer compositions such as carboxymethyl cellulose, carboxyethyl cellulose, gelatin, etc. The following is a typical developer solution given to illustrate but not limit my invention.

2-amino-5-diethylaminotoluene HCl	2.0 g.
Sodium sulfite (anhydrous)	2.0 g.
Sodium carbonate monohydrate	20.0 g.
Potassium bromide	1.0 g.
Coupler	2.0 g.
Water to 1000 ml.	

The other coupler examples used to illustrate my invention are nondiffusing and are used to advantage in photographic emulsion layers. Couplers, such as 2, 12, 14, 15, 16, 17, 18, 24, and 25 illustrate those that are incorporated as Fischer-type couplers. The other nondiffusing couplers, e.g., 3, 8, 9, 10, 11, 13, 21, and 22, are incorporated in emulsion layers by methods such as are described by Mannes et al., U.S. Patent 2,304,939, issued December 15, 1942, Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, etc., in which high-boiling organic solvents are used to dissolve the coupler, and by methods described in Vittum et al. U.S. Patent 2,801,170, and Fierke et al. U.S. Patent 2,801,171, both issued July 30, 1957, and Julian U.S. Patent 2,949,360, issued Aug. 16, 1960, in which low-boiling or water-soluble organic solvents are used with or in place of the high-boiling solvent. The use of such coupler dispersions permits thinner emulsion layers. These thinner layers are very desirable because they cause less light scattering, consequently they produce sharper images.

Coupler 17 contains a preformed dye attached to the coupler on the aryloxy group. This dye is eliminated on the coupling of the coupler with an oxidized color developer and diffuses out of the film. This coupler can be used as a yellow-colored coupler for the purpose of correcting for the unwanted blue absorption of the cyan image dyes, i.e., that formed from the coupler itself as well as that formed from other cyan couplers. Generally, such a coupler as this would be used in combination with another image-forming cyan coupler in the same layer.

My couplers are used to advantage in the color development of photographic hydrophilic colloid-silver halide emulsion layers of the developing-out type in the emulsion layer or a contiguous layer. The emulsions may contain silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc., as the light-sensitive material.

Any of the hydrophilic colloids used in photographic elements are used to advantage, including gelatin, colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound, etc.

The emulsions used in the photographic element of my invention can be chemically or optically sensitized.

The couplers of my invention may also be used to advantage in image-forming layers, either alone or with image-forming compounds other than silver halide, such as ZnO, ZnS, CdS, CdSe, NiS, etc., either with or without binders such as gelatin, polyvinyl alcohol, etc.

Usually my emulsions are coated on photographic supports in the form of multilayer color photographic elements wherein at least three differently sensitized emulsion layers are coated over one another on the support. Usually the support is coated in succession with a red-sensitive layer, a green-sensitive layer, and a blue-sensitive layer either with or without a Carey Lea silver yellow filter layer between the blue-sensitive and green-sensitive layers. The three differently color sensitized layers may be arranged in any other order over one another that is desirable; however, the Carey Lea filter layer obviously would not be put over the blue-sensitive layer. Preferably, these light-sensitive layers are arranged on the same side of the support.

My invention is further illustrated by the following typical examples.

Example 1

Samples of a single layer relatin silver bromo-iodide coating were exposed (i.e., for $\frac{1}{25}$ -second on a 1B intensity scale sensitometer). These strips were then processed to color positives by the following process; all process temperatures were 68°.

	Minutes
MQ Developer	5
Kodak F-5 Fixing Bath	5
Re-exposure (i.e., 12" 100 watt bulb)	1
Color Developer (formula below)	10
Kodak F-5 Fixing Bath	5
Water Wash	5
Bleach (ferricyanide)	5
Water Wash	5
Kodak F-5 Fixing Bath	5
Water Wash	10
Dry	--

Developer formula

Benzyl alcohol	ml----	4
Sodium hexametaphosphate	-----g----	0.5
Sodium sulfite desiccated	-----g----	2.0
Sodium hydroxide	-----g----	0.16
Coupler ¹	-----g----	2.0
4 - amino - 3 - methyl - N - ethyl - N - [β - methane-sulfonamido)ethyl]aniline sesquisulfate hydrate	g-----	5.0
Sodium carbonate monohydrate	-----g----	50.0
Sodium bromide	-----g----	0.2
Water to 1 liter.		
pH to 10.75.		

¹ The couplers used in the above-mentioned developer formula were Couplers 1, 4, 5, 6, 7, 19, and 20, respectively.

Good cyan dye images were formed in each of the respective strips.

Example 2

Single layer gelatin silver bromoiodide coatings were prepared containing Couplers 3, 8, 9, 10, 11, 13, 21, and 22, respectively. Each of these couplers were dispersed in said coatings in the from of a finely-dispersed solution of the coupler in coupler solvent, di-n-butylphthalate. These coatings contained 10 parts of gelatin, 5 parts of silver, 2 parts of coupler, and 1 part of coupler solvent. Samples of the above-mentioned coatings were given $\frac{1}{25}$ second exposure on a 1B intensity scale sensitometer and processed in a conventional manner to color negatives, respectively, using the following developer solution.

Sodium sulfite (anhydrous)	-----	G. 2.0
2-amino-5-diethylaminotoluene HCl	-----	2.0
Sodium carbonate monohydrate	-----	20.0
Potassium bromide	-----	2.0
Water to 1 liter.		
pH to 10.86.		

Each of the processed strips contained high quality cyan dye images having good heat and light stability and low fog.

Similarly, other couplers of my invention are used to advantage in color photography as illustrated previously with representative couplers. Further, the couplers of my invention are valuable as cyan image-forming couplers in multilayer photographic color films containing other classes of couplers in the other layers of said film. Such other couplers are, for example, yellow image-forming couplers containing a methylene or substituted methylene group having two carbonyl groups directly attached thereto, and magenta image-forming couplers such as 5-pyrazolones, cyanoacetyl coumarones, etc.

In general, my couplers are the product of the reaction of a 1-hydroxy-4-aryloxy-2-naphthoyl chloride with the appropriately substituted amine.

Alternatively, my couplers may be prepared by reacting 1-hydroxy-4-acetoxy-2-naphthoyl chloride with an amine, converting the resultant 1-hydroxy-4-acetoxy-2-naphthamide to the 1-benzyloxy-4-acetoxy-2-naphthamide, hydrolyzing to the corresponding 4-hydroxy compound, the sodium salt of which is then reacted with the fluorobenzene. This 1-benzyloxy-4-aryloxy-2-naphthamide is then converted to the corresponding 1-hydroxy-4-aryloxy-2-naphthamide by hydrogenolysis of the 1-benzyloxy group.

The following preparations will illustrate the various methods which were used to prepared my cyan-forming two-equivalent couplers.

Preparation of Coupler 2, 1-hydroxy-4-{4-[α -(3-pentadecylphenoxy)butyramido]phenoxy}-N-octadecyl-3',5'-dicarboxy-2-naphthanilide

Intermediate 1—1-hydroxy - 4 - (4-nitrophenoxy)-2-naphthoic acid: To a solution of 20 g. of 1,4-dihydroxy-2-naphthoic acid in 150 ml. of dimethyl formamide was added 20 g. of aqueous 40% sodium hydroxide solution and 14 g. of 4-nitrofluorobenzene over a period of 5 minutes with stirring under a nitrogen atmosphere. The reaction mixture was stirred for a total of 2 hours, after which time it was poured into dilute hydrochloric acid whereupon a solid separated, was collected, recrystallized twice from methyl alcohol, to yield the product.

Intermediate 2—1-hydroxy - 4 - (4-nitrophenoxy)-2-naphthoyl chloride: A mixture of 3.25 g. of Intermediate 1 above in 10 ml. of thionyl chloride was stirred at room temperature for 2 hours, during which time all of the acid dissolved and a yellow solid separated, was collected, and recrystallized from warm anhydrous acetonitrile to yield the product.

Intermediate 3—1-hydroxy-4-(4-nitrophenoxy)-N-octadecyl-3',5'-dicarbomethoxy-2-naphthanilide: To a solution of 2.4 g. of Intermediate 2 above in 100 ml. of anhydrous dioxane was added 3.4 g. of N-octadecyl-3,5-dicarbomethoxyaniline and 1 ml. of N,N-dimethylaniline. The clear reaction mixture was held at room temperature overnight, after which time it was poured into 500 ml. of cold water, whereupon an oil separated which solidified on additional water washing. The solid was collected and recrystallized twice from acetonitrile to yield the product.

Intermediate 4—1 - hydroxy-4-(4-aminophenoxy)-N-octadecyl-3',5'-dicarbomethoxy-2-naphthanilide: A solution of 1.6 g. of Intermediate 3 above in 100 ml. of absolute ethyl alcohol was reduced on the Parr hydrogenation apparatus using Raney nickel as the catalyst. After the reduction had been completed and the catalyst removed

by filtration, the filtrate was concentrated in vacuo and the solid residue was recrystallized from acetonitrile to yield the product.

Intermediate 5—1-hydroxy-4-{4-[α -(3-pentadecylphenoxy)butylamido]phenoxy}-N-octadecyl-3',5'-dicarbomethoxy-2-naphthanilide: To a solution of 3.5 g. of Intermediate 4 above and an excess of sodium acetate in 50 ml. of acetic acid was added a solution of 2 g. of α -(3-pentadecylphenoxy)butyl chloride in 25 ml. of acetic acid with stirring at room temperature. After stirring the reaction mixture for 1 hour, it was heated to 60° C. and held at room temperature overnight. The mixture was then poured into 500 ml. of cold water whereupon a solid separated, was collected and dried to yield the product.

Coupler 2—Named above: To a solution of Intermediate 5 above in 250 ml. of absolute ethyl alcohol was added a solution of 6 g. of sodium hydroxide in 100 ml. of water over a period of 2 minutes with vigorous stirring. The mixture was stirred at 65° C. for 1½ hours, after which time it was poured into 1 liter of water containing 25 ml. of concentrated hydrochloric acid. The solid which separated was collected, washed with cold water, dried, and recrystallized twice from acetonitrile to yield the product.

Preparation of Coupler 3, 1-hydroxy-4-(4-nitrophenoxy)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide)

To a solution of 17 g. of δ -(2,4-di-t-amylphenoxy)-butylamine and 6 ml. of dimethylaniline in 200 ml. of anhydrous dioxane was added 18 g. of 1-hydroxy-4-(4-nitrophenoxy)-2-naphthoyl chloride (Intermediate 2, Coupler 2 above) with stirring. The reaction mixture was stirred overnight at room temperature, after which time it was poured into 1 liter of cold water containing 5 ml. of acetic acid whereupon a solid separated, was collected, washed with cold water, and dried. The solid was recrystallized from a mixture of hexane and benzene to yield the product.

Preparation of Coupler 24, 1-hydroxy-4-(4-acetamidophenoxy)-N-octadecyl-3',5'-dicarboxy-2-naphthanilide

Intermediate—1-hydroxy-4-(4-acetamidophenoxy)-N-octadecyl-3',5'-dicarbomethoxy-2-naphthanilide: To a

solution of 9.6 g. of 1-hydroxy-4-(4-aminophenoxy)-N-octadecyl-3',5'-dicarbomethoxy-2-naphthanilide (Intermediate 4, Coupler 2 above) and 1.5 g. of anhydrous sodium acetate in 100 ml. of acetic acid was added 1.1 g. of acetyl chloride with stirring. The reaction mixture was stirred at room temperature for 1 hour, after which time it was poured into 800 ml. of water whereupon a solid separated, was collected, and air dried. This solid was recrystallized from acetonitrile to yield the product.

Coupler 24—Named above: To a solution of 3 g. of the Intermediate above in 50 ml. of ethyl alcohol was added 2 ml. of aqueous 40% sodium hydroxide. An additional 5 ml. of water was added and the solution was stirred for 2 hours. The resultant solution was added to 200 ml. of 5% hydrochloric acid whereupon a solid separated, was collected, washed with water, and dried. This solid was recrystallized twice from acetonitrile to yield the product.

Preparation of Coupler 25, 1-hydroxy-4-(4-nitrophenoxy)-N-octadecyl-3',5'-disulfo-2-naphthanilide disodium salt

Intermediate—1-hydroxy-4-(4-nitrophenoxy)-N-octadecyl-3',5'-difluorosulfonyl-2-naphthanilide: To a solution of 1.3 g. of 1-hydroxy-4-(4-nitrophenoxy)-2-naphthoyl chloride (Intermediate 2, Coupler 2 above) and 10 drops of dimethylaniline in 20 ml. of anhydrous dioxane was added 1.4 g. of N-octadecyl-3,5-difluorosulfonylaniline with stirring. This mixture was stirred overnight at room temperature, after which time it was poured into 150 ml. of dilute acetic acid whereupon a solid separated, was collected, and recrystallized twice from acetonitrile to yield the product.

Coupler 25—Named above: The Intermediate above was converted to the sodium salt in a manner similar to that used to prepare Coupler 24 above.

The other couplers of my invention were each prepared in accordance with the procedure used to prepare Coupler 3 using the respective intermediates given in the following table.

TABLE

Coupler No.:	Acid Chloride Intermediate	Amine Intermediate
1	1-hydroxy-4-(4-methylsulfonylphenoxy)-2-naphthoyl chloride	Ammonia.
4	1-hydroxy-4-(2,4-dinitrophenoxy)-2-naphthoyl chloride	Ethylamine.
5	1-hydroxy-4-phenoxy-2-naphthoyl chloride	2-methoxyaniline.
6	1-hydroxy-4-(4-nitrophenoxy)-2-naphthoyl chloride	Phenethylamine.
7	do.	β -(2-nitrophenyl)-ethylamine. ¹
8	1-hydroxy-4-(pentafluorophenoxy)-2-naphthoyl chloride	β -(4-nitrophenyl)-ethylamine. ²
9	1-hydroxy-4-(1-naphthoxy)-2-naphthoyl chloride	Diethylamine.
10	1-hydroxy-4-acetoxy-2-naphthoyl chloride	4-(4-t-butylphenoxy)-aniline. ³
11	1-hydroxy-4-(4-chlorophenoxy)-2-naphthoyl chloride	2-tetradecyloxyaniline.
12	1-hydroxy-4-(4-(N-methyl-N-propylsulfamyl)phenoxy)-2-naphthoyl chloride	N-octadecyl-3,5-dicarbomethoxyaniline. ⁴
13	1-hydroxy-4-(4-(4-hydroxyphenylsulfonyl)phenoxy)-2-naphthoyl chloride	3-nitroaniline. ⁵
14	1-hydroxy-4-(4-nitro-3-pentadecylphenoxy)-2-naphthoyl chloride	N-octadecyl-4-sulfoaniline sodium salt.
15	1-hydroxy-4-(3-nitrophenoxy)-2-naphthoyl chloride	N-octadecyl-3,5-dicarbomethoxyaniline. ⁶
16	1-hydroxy-4-phenoxy-2-naphthoyl chloride	β -(4-nitrophenyl)-ethylamine. ⁷
17	1-hydroxy-4-acetoxy-2-naphthoyl chloride	4-(4-t-butylphenoxy)-aniline. ⁸
18	1-hydroxy-4-(4-chlorosulfonylphenoxy)-2-naphthoyl chloride	Octadecylamine. ⁹
19	1-hydroxy-4-phenoxy-2-naphthoyl chloride	Morpholine.
20	1-hydroxy-4-(4-nitrophenoxy)-2-naphthoyl chloride	Cyclohexylamine.
21	4,4'-bis(1-hydroxy-2-chlorocarbonyl-4-naphthoxy)-diphenylsulfone	Ethylamine. ¹⁰
22	1,4-bis(1-hydroxy-2-chlorocarbonyl-4-naphthoxy)-benzene	2-nitroaniline. ¹¹
23	1-hydroxy-4-(4-chlorosulfonylphenoxy)-2-naphthoyl chloride	N-methyl-aniline. ¹¹
26	1-hydroxy-4-phenoxy-2-naphthoyl chloride	2-aminobenzimidazole.
27	1-hydroxy-4-(4-nitrophenoxy)-2-naphthoyl chloride	N-ethylmethylaniline.
28	1-hydroxy-4-phenoxy-2-naphthoyl chloride	Dimethylamine.

¹ The nitro product was catalytically reduced and the two amino groups were acetylated using acetic anhydride to yield Coupler 7.

² The nitro intermediate was then catalytically reduced and the resultant amino compound was acetylated with α -(2,4-di-t-amylphenoxy)-acetyl chloride to yield Coupler 8.

³ The intermediate, 1-hydroxy-4-acetoxy-4'-(4-t-butylphenoxy)-2-naphthanilide was converted to the corresponding 1-benzoyloxy derivative, hydrolyzed to the corresponding 4-hydroxy derivative, converted to the 4-pyridyloxy derivative (i.e., using 4-fluoropyridine), and then converted to Coupler 10 by the hydrogenolysis of the 1-benzoyloxy group.

⁴ The ester intermediate was then hydrolyzed to yield Coupler 12.

⁵ The nitro intermediate was catalytically reduced and acetylated with α -(3-pentadecylphenoxy)-butyl chloride to yield Coupler 13.

⁶ The ester intermediate was hydrolyzed to yield Coupler 15.

⁷ The nitro intermediate was catalytically reduced and acetylated with 2-(2,4-di-t-amylphenoxy)-5-nitrobenzoyl chloride. The second nitro

intermediate was also catalytically reduced and acetylated with 3,5-di-chlorosulfonylbenzoyl chloride. The chlorosulfonyl groups were hydrolyzed to the sulfonic acid sodium salts to yield Coupler 16.

⁸ The intermediate, 1-hydroxy-4-acetoxy-4'-(4-t-butylphenoxy)-2-naphthanilide, was converted to the corresponding 1-benzoyloxy derivative, hydrolyzed to the corresponding 4-hydroxy derivative, and converted to the 4-[4-(4-sulfophenylazo)phenoxy] derivative (i.e., using 4-(4-fluorophenylazo)-benzene sulfonic acid), and then converted to Coupler 17 by the hydrogenolysis of the 1-benzoyloxy group.

⁹ The chlorosulfonyl intermediate was converted to Coupler 12 by alkaline hydrolysis.

¹⁰ The nitro intermediate was catalytically reduced and acetylated with acetic anhydride to yield Coupler 22.

¹¹ The intermediate containing the chlorosulfonyl group was hydrolyzed (i.e., by alkaline hydrolysis) to yield Coupler 23.

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The two-equivalent image-forming couplers of my invention are distinguished from other two-equivalent couplers by having an aryloxy group substituted on the coupling position of the coupler molecule. My couplers are characterized by not producing color fog, a problem with certain prior art two-equivalent couplers, and by having very good coupling reactivity. Further, my novel couplers form dye images which exhibit very good heat and light stability when they are incorporated into photographic coatings relative to that exhibited by many of the prior art couplers.

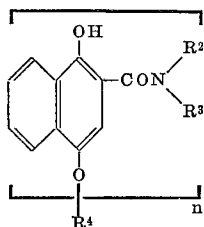
My couplers are dispersed readily in emulsion layers as a coupler solvent solution having a wide range of coupler-to-solvent ratios.

My couplers are not only valuable for the reasons cited, but because photographic emulsion layers coor developed with them require only one-half the amount of silver halide required by four-equivalent couplers. Of particular value are certain of my nondiffusing couplers which have high coupling reactivity when dispersed in photographic emulsion layers without any high-boiling solvent. These couplers are coated to advantage in particularly thin layers that produce good sharp images. The couplers of my invention may be used in emulsion layers or color developer solutions either alone or admixed with other couplers, either four- or two-equivalent couplers, competing couplers, and the like.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. An image-forming layer containing silver halide and a coupler of the formula:

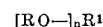


wherein n represents an integer of from 1 to 2; R^2 and R^3 each represents a group selected from the class consisting of the hydrogen atom, an alkyl radical, an aryl radical, a heterocyclic radical, and, together, the non-metallic atoms necessary to complete a heterocyclic ring; R^4 represents an aryl group selected from the class consisting of a phenyl group, a naphthyl group, a pyridyl group, a quinolyl group, a phenylene group, a naphthylene group, a pyridylene group and a quinolyne group such that when n represents the integer 1, R^4 represents an aryl group selected from the class consisting of a phenyl group, a naphthyl group, a pyridyl group and a quinolyl group in which a carbon atom in a ring of said aryl group is attached directly to the oxygen atom attached to the 4 carbon atom of the 1-hydroxy-2-naphthamide ring shown inside the brackets of said formula, and and such that when n represents the integer 2, R^4 represents an aryl group selected from the class consisting of a phenylene group, a naphthylene group, a pyridylene group and a quinolyne group in which one carbon atom in a ring of said aryl group is attached directly to the oxygen atom attached to the 4 carbon atom of one of the 1-hydroxy-2-naphthamide rings shown inside the brackets of said formula and in which another carbon atom in a ring of said aryl group is attached directly to the oxygen atom attached to the 4 carbon atom in the other 1-hydroxy-2-naphthamide ring shown inside the brackets of said formula.

2. In a multilayer multicolor element containing silver halide and incorporated color-forming couplers, the im-

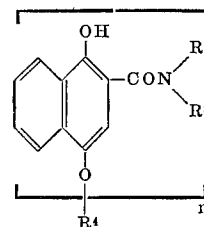
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provement wherein at least one such coupler comprises a cyan-dye-forming coupler which is capable of forming a cyan dye on coupling with the oxidation product of an aromatic amino developing agent, said cyan-dye-forming coupler being selected from those having the formula:



wherein R represents a 4-hydroxy-3-carbamyl-1-naphthyl group; n represents an integer of from 1 to 2; and R^1 represents an aryl group selected from the class consisting of a phenyl group, a naphthyl group, a pyridyl group, a quinolyl group, a phenylene group, a naphthylene group, a pyridylene group and a quinolyne group, such that when n represents the integer 1, R^1 represents an aryl group selected from the class consisting of a phenyl group, a naphthyl group, a pyridyl group and a quinolyl group, in which a carbon atom in a ring of said aryl group is attached directly to the oxygen atom in said formula, and such that when n represents the integer 2, R^1 represents an aryl group selected from the class consisting of a phenylene group, a naphthylene group, a pyridylene group and a quinolyne group in which one carbon atom in a ring of said aryl group is attached directly to one of the oxygen atoms of said formula and in which another carbon atom in a ring of said aryl group is attached directly to the other oxygen atom of said formula.

3. In a multilayer multicolor element containing silver halide and incorporated color formers, the improvement wherein at least one such color former comprises a cyan-dye-forming coupler of the formula:



wherein n represents an integer of from 1 to 2; R^2 and R^3 each represents a group selected from the class consisting of the hydrogen atom, an alkyl radical, an aryl radical, a heterocyclic radical, and, together, the non-metallic atoms necessary to complete a heterocyclic ring; R^4 represents an aryl group selected from the class consisting of a phenyl group, a naphthyl group, a pyridyl group, a quinolyl group, a phenylene group, a naphthylene group, a pyridylene group and a quinolyne group such that when n represents the integer 1, R^4 represents an aryl group selected from the class consisting of a phenyl group, a naphthyl group, a pyridyl group and a quinolyl group in which a carbon atom in a ring of said aryl group is attached directly to the oxygen atom attached to the 4 carbon atom of the 1-hydroxy-2-naphthamide ring shown inside the brackets of said formula, and such that when n represents the integer 2, R^4 represents an aryl group selected from the class consisting of a phenylene group, a naphthylene group, a pyridylene group and a quinolyne group in which one carbon atom in a ring of said aryl group is attached directly to the oxygen atom attached to the 4 carbon atom of one of the 1-hydroxy-2-naphthamide rings shown inside the brackets of said formula and in which another carbon atom in a ring of said aryl group is attached directly to the oxygen atom attached to the 4 carbon atom in the other 1-hydroxy-2-naphthamide ring shown inside the brackets of said formula.

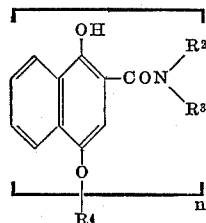
4. In an image-forming layer containing silver halide and a cyan-dye-forming coupler that is capable of forming a cyan dye on coupling with the oxidation product of an aromatic amino developing agent, the improvement

wherein said coupler is selected from those having the formula:



wherein R represents a 4-hydroxy-3-carbamyl-1-naphthyl group; n represents an integer of from 1 to 2; and R^1 represents an aryl group selected from the class consisting of a phenyl group, a naphthyl group, a pyridyl group, a quinolyl group, a phenylene group, a naphthylene group, a pyridylene group and a quinolyne group, such that when n represents the integer 1, R^1 represents an aryl group selected from the class consisting of a phenyl group, a naphthyl group, a pyridyl group and a quinolyl group, in which a carbon atom in a ring of said aryl group is attached directly to the oxygen atom in said formula, and such that when n represents the integer 2, R^1 represents an aryl group selected from the class consisting of a phenylene group, a naphthylene group, a pyridylene group and a quinolyne group in which one carbon atom in a ring of said aryl group is attached directly to one of the oxygen atoms of said formula and in which another carbon atom in a ring of said aryl group is attached directly to the other oxygen atom of said formula.

5. In an image-forming layer containing silver halide and a cyan-dye-forming coupler, the improvement wherein the said coupler comprises a coupler of the formula:



wherein n represents an integer of from 1 to 2; R^2 and R^3 each represents a group selected from the class consisting of the hydrogen atom, an alkyl radical, and aryl radical, a heterocyclic radical, and, together, the non-metallic atoms necessary to complete a heterocyclic ring; R^4 represents an aryl group selected from the class consisting of a phenyl group, a naphthyl group, a pyridyl

group, a quinolyl group, a phenylene group, a naphthylene group, a pyridylene group and a quinolyne group such that when n represents the integer 1, R^4 represents an aryl group selected from the class consisting of a phenyl group, a naphthyl group, a pyridyl group and a quinolyl group in which a carbon atom in a ring of said aryl group is attached directly to the oxygen atom attached to the 4 carbon atom of the 1-hydroxy-2-naphthamide ring shown inside the brackets of said formula, and such that when n represents the integer 2, R^4 represents an aryl group selected from the class consisting of a phenylene group, a naphthylene group, a pyridylene group and a quinolyne group in which one carbon atom in a ring of said aryl group is attached directly to the oxygen atom attached to the 4 carbon atom of one of the 1-hydroxy-2-naphthamide rings shown inside the brackets of said formula and in which another carbon atom in a ring of said aryl group is attached directly to the oxygen atom attached to the 4 carbon atom in the other 1-hydroxy-2-naphthamide ring shown inside the brackets of said formula.

6. A light-sensitive hydrophilic colloid silver halide emulsion containing 1-hydroxy-4-(1-naphthyloxy)-N,N-diethyl-2-naphthamide.

7. A light-sensitive hydrophilic colloid-silver halide emulsion containing 1-hydroxy-4-(pentafluorophenoxy)-N-{ β - {4 - [α -(2,4-di-t-amylphenoxy)acetamido]phenyl} ethyl}-2-naphthamide.

8. A light-sensitive hydrophilic colloid-silver halide emulsion layer containing 1-hydroxy-4-(4-nitrophenoxy)-N-[β -2,4-di-t-amylphenoxy]butyl]-2-naphthamide.

9. A light-sensitive hydrophilic colloid-silver halide emulsion containing 1-hydroxy-4-(4-chlorophenoxy)-2'-tetradecyloxy-2-naphthanilide.

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J. TRAVIS BROWN, Primary Examiner

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